

The role of matrix material and CCl_4 (electron acceptor) on the ionization mechanisms of matrix-isolated naphthalene

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The important role of large molecular ions—and specifically of polycyclic aromatic hydrocarbons (PAHs)—in astrophysics has been recently recognized.¹ In an attempt to provide spectroscopic data on PAH ions under conditions relevant to astrophysical applications, we have undertaken a systematic study of the formation mechanisms and optical properties of PAH ions isolated in argon and neon matrices.² Neon matrices perturb the electronic spectra of the trapped species very little^{3,4} and, thus, are most representative of the environment surrounding cold free, gas phase molecules in the interstellar medium.

In our previous experiments,² the naphthalene cation was formed by direct, one-photon ionization (PI) of the neutral molecule isolated in an inert gas matrix at 4.2 K. The photon energy of 10.2 eV is well above the 8.15 eV first ionization potential of C_{10}H_8 .⁵ The ultraviolet-visible absorption spectrum of the $\text{C}_{10}\text{H}_8^+$ cation, formed under these conditions [Fig. 1(a)], consists of weak bands due to the low oscillator strengths of the corresponding vibronic transitions and the charge saturation effect^{2,3(a)} which limits the ion yield. To optimize the yield of $\text{C}_{10}\text{H}_8^+$ in neon matrices and to test if the continuum absorption observed is associated with the naphthalene cation we have added CCl_4 as an electron acceptor to the sample.

In this note, we summarize the original results obtained when CCl_4 is included in the naphthalene/neon matrices. $\text{C}_{10}\text{H}_8/\text{CCl}_4/\text{Ne}$ matrices of relative concentrations 1:4:1000 and 1:2:600 were prepared using the techniques described in Ref. 2.

(1) Upon irradiation of the matrix with 10.2 eV photons, a very strong [Absorbance (A) = 0.3], broad absorption band (FWHM = $4800 \pm 60 \text{ cm}^{-1}$) peaking at 408 nm is produced, together with the much weaker visible band system associated with the naphthalene cation^{2,6} [Fig. 1(b)]. Based on electron spin resonance (ESR) spectroscopy^{7(a)} and matrix isolation spectroscopy^{7(b)} studies we attribute this strong 408 nm absorption in a neon matrix to the dissociative transition $\text{C} \leftarrow \text{X}$ of CCl_4^+ . It has been shown^{7(a)} that the released chlorine atom is stabilized in the solid at low temperature by making a weak three electron bond with a Cl atom in the released CCl_3^+ group [$[\text{CCl}_3^+ \cdots \text{Cl}]$ complex]. Compare the 408 nm peak position in neon to the 410 nm absorption in the pure solid^{7(a)} and to the 425, 430, and 455 nm absorptions previously measured in argon, krypton, and xenon matrices, respectively.^{7(b)}

(2) Irradiation of neon matrices containing C_{10}H_8 and CCl_4 with 10.2 eV photons leads to the ionization of both species as indicated above, however the yield of $\text{C}_{10}\text{H}_8^+$ is severely limited compared to a sample without CCl_4 [compare Figs. 1(a) and 1(b)]. This indicates that the forma-

tion of CCl_4^+ —which is far more efficient than the formation of $\text{C}_{10}\text{H}_8^+$ —induces charge saturation in the matrix^{2,3(a)} which limits further formation of $\text{C}_{10}\text{H}_8^+$.

(3) In an attempt to circumvent this limitation on the number of naphthalene cations produced in the matrix when using 10.2 eV photons, we have utilized the multiphoton ionization (MPI) technique.^{5,6,8} In this case, a 100 W, medium-pressure Hg arc (5.6–1.2 eV output) was used. Under these conditions, *no absorptions* were produced in the 300–900 nm range after irradiation of $\text{C}_{10}\text{H}_8/\text{CCl}_4/\text{Ne}$ matrices [Fig. 1(c)] for variable amounts of time up to 40 min. *In sharp contrast, however, the naphthalene cation yield was greatly enhanced when the experiment was repeated in an argon matrix* [$\text{C}_{10}\text{H}_8/\text{CCl}_4/\text{Ar} = 1:3:800$; Fig. 1(d)]. The presence of CCl_4 in the argon matrix increased the $\text{C}_{10}\text{H}_8^+$ bands by a factor of

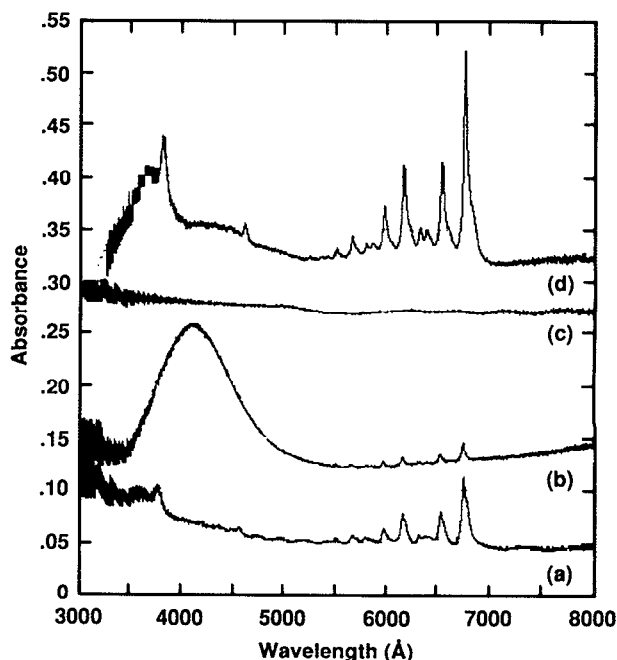


FIG. 1. (a) The absorption spectrum of the naphthalene cation in a neon matrix. Experimental conditions: Naphthalene/Ne = 1:600, 4.2 K, 20 min VUV irradiation with 10.2 eV photons (H_2 -flow discharge lamp). (b) The absorption spectra of CCl_4^+ and $\text{C}_{10}\text{H}_8^+$ in a neon matrix. Experimental conditions: Naphthalene/ CCl_4 /Ne = 1:2:600, 4.2 K, 20 min VUV irradiation with 10.2 eV photons (H_2 -flow discharge lamp). (c) Experimental conditions: Naphthalene/ CCl_4 /Ne = 1:2:600, 4.2 K, 18 min UV irradiation with 5.6 eV photons (medium-pressure Hg lamp). Contrast this to (d). (d) Experimental conditions: Naphthalene/ CCl_4 /Ar = 1:3:800, 4.2 K, 30 min UV irradiation with 5.6 eV photons (medium-pressure Hg lamp). Contrast this to (c). Note: For the clarity of the figure, the base lines of spectra (b), (c), and (d) were shifted by 0.05, 0.25, and 0.30 absorbance units, respectively.

3 [compare Figs. 1(d) and 1(a)]. This result is in good agreement with the previous argon-matrix study of Andrews *et al.*⁶ Moreover, no CCl_4^+ absorption was observed in the 300–900 nm range.

These experimental results suggest the following. (i) The electron acceptor molecules must possess an ionization potential significantly higher than the energy of the irradiating photons. This is illustrated by the low yield of naphthalene cations measured when the electron acceptor is either produced by photodissociation (C_2H_2 in Ref. 2) or ionized (CCl_4 in this study). (ii) The absorption frequency of CCl_4^+ is strongly related to the polarizability of the surrounding medium as indicated by the redshift of 0.12 eV of the $\text{C}-\text{X}$ electronic transition when going from Ne to Ar (a redshift of 0.31 eV is observed when going from Ne to Xe). This is further illustrated by the dependence of the peak position of CCl_4^+ on the initial CCl_4 concentration in the matrix (408 nm for 0.3% CCl_4 in Ne and 414 nm for 0.4% CCl_4 in Ne). These effects reflect the variation in strength of the $\text{Cl}\cdots\text{Cl}$ three electron bond of the $[\text{CCl}_3^+ \cdots \text{Cl}]$ complex.^{7(a)} (iii) The absorption frequencies of the visible and ultraviolet bands of $\text{C}_{10}\text{H}_8^+$ trapped in an argon matrix containing CCl_4 compared with those of $\text{C}_{10}\text{H}_8^+$ isolated in an argon matrix with no electron acceptor present² show that there is a small but measurable consistent blue shift of the energy levels on the order of $10\text{--}20\text{ cm}^{-1}$. This shift should be corrected for when measuring the naphthalene cation absorption transitions in doped argon matrices. (iv) In our previous study of the naphthalene cation in argon and neon matrices, a strong, broad continuum—extending from about 510 to 330 nm—accompanied the spectrum of the cation.² While all of the discrete spectral features formed upon irradiation of the neutral C_{10}H_8 were unequivocally attributed to the cation $\text{C}_{10}\text{H}_8^+$, it was not clear if the continuum was also associated with the cation, its anionic counterpart ($\text{C}_{10}\text{H}_8^-$) or the neutral molecule interacting with the charge field in the matrix. The observation of the same continuous absorption when CCl_4 is used as an electron acceptor *rules out* the naphthalene anion ($\text{C}_{10}\text{H}_8^-$) as a carrier of the continuum. Moreover, the fact that the continuum correlates well with the known cation bands [compare, for example, Figs. 1(a), 1(c), and 1(d)], following either one or two-photon ionization mechanisms, indicates that the naphthalene cation is indeed responsible for this feature. This attribution of the continuum to the cation has significant astrophysical consequences.⁹ (v) The failure to form $\text{C}_{10}\text{H}_8^+$ by irradiation of $\text{C}_{10}\text{H}_8/\text{CCl}_4/\text{Ne}$ solid samples with 5.6 eV energy photons, while the same energy photons yield $\text{C}_{10}\text{H}_8^+$ in an argon matrix, pinpoints a strong *spin-orbit coupling effect* induced by the matrix material. The MPI scheme, used to explain the formation of $\text{C}_{10}\text{H}_8^+$ with photons of lower energy than the ionization potential of naphthalene, requires the population of an intermediate state in the transition from the neutral to the ion.^{5,8} In this energy range, argon-matrix isolated naphthalene shows two absorptions at 3.95 eV (weak) and 4.37 eV (strong) corresponding to the excitation of the S_1 ($^1B_{3u}$) and S_2 ($^1B_{2u}$) singlet states, respectively.² The lowest triplet state T_1 ($^3B_{2u}$) of 4.2 K-

crystalline naphthalene is situated at 2.63 eV.¹⁰ It was suggested⁸ that reabsorption from the populated S_1 ($^1B_{3u}$) state of neutral naphthalene combined perhaps with the much less favorable absorption from the populated triplet T_1 ($^3B_{2u}$) state produced the ionization. (In the earlier experiments,⁸ photolysis was carried out with a 1000 W, high-pressure Hg lamp). Our experiments, which compare the ionization mechanism in a neon matrix with that in an argon matrix clearly indicate that under our low flux conditions the two-photon ionization process can occur *only* through the *triplet* state. The $(S_0) \leftarrow (S_1)$ and $(S_0) \leftarrow (S_2)$ radiative relaxation rates are at least two orders of magnitude faster than the photon pumping rate possible with the 100 W lamp used.

Two mechanisms involving a triplet intermediate are plausible: (i) $^2A_u(D_0) \leftarrow ^3B_{2u}(T_1) \leftarrow X^1A_g(S_0)$. In this process, the first step is spin forbidden but may be induced in an argon (or heavier atom) matrix. Alternatively, or simultaneously, a three-step mechanism is also possible: (ii) $^2A_u(D_0) \leftarrow ^3B_{2u}(T_1) \leftarrow -(ISC) - ^1B_{2u}(S_2) \leftarrow X^1A_g(S_0)$. The intersystem crossing (ISC) transition is facilitated by the spin-orbit coupling induced by the matrix material. The population of the triplet $^3B_{2u}(T_1)$ state of neutral naphthalene under our experimental conditions is supported by the strong green phosphorescence¹¹ [$X^1A_g(S_0) \leftarrow ^3B_{2u}(T_1)$] characteristic of naphthalene observed following irradiation of the argon matrix with 5.6 eV photons. In the case of a neon matrix, where no ISC is favored, the excited singlet state apparently resonantly radiates to the ground state before reabsorption of a second photon and, consequently, ionization cannot be achieved. These results illustrate the strong influence of the matrix material on the competing radiative (fluorescence and/or phosphorescence) and nonradiative (internal conversion and/or intersystem crossing) relaxation processes of the trapped molecule.

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